

Supplementary Materials

Tuning the linear and nonlinear optical properties of pyrene-pyridine chromophores by protonation and complexation to d¹⁰ metal centers

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Experimental Procedures

1. General Information

All reagents were purchased from chemical suppliers and used without further purification unless otherwise stated. **L**₂ was prepared according to literature procedures.^{S1}

¹H NMR spectra were recorded on a Bruker AVANCE-400 instrument (400 MHz). Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak (CDCl₃, ¹H 7.28 ppm; DMSO, ¹H 2.50 ppm). UV-Visible spectra were collected by a Shimadzu UV3600 spectrophotometer. Steady state emission spectra were obtained using a FLS 980 (Edinburg Instrument Ltd) equipped with a 450 W Xenon arc lamp.

The molecular first hyperpolarizabilities of the compounds were measured by the solution phase dc EFISH method,^{S2} which can provide direct information on the intrinsic molecular SHG responses, γ_{EFISH} thorough:

$$\gamma_{\text{EFISH}} = \frac{\mu\beta_{\lambda}}{5KT} + \gamma(-2\omega; \omega, \omega, 0)$$

$\mu\beta/5kT$ is the dipolar orientational contribution, and $\gamma(-2\omega; \omega, \omega, 0)$, the third-order term at frequency ω of the incident light, is the electronic contribution to γ_{EFISH} , which is negligible for molecules of the type investigated here.

During the EFISH measurements, upon cell translation, the intensity of the second harmonic radiation is modulated as interference fringes (Maker fringes). The width and the periodicity of the fringes are correlated to the macroscopic susceptibility $\Gamma(S)$ of the solution that depends on $I_{2\omega}$ and on the coherence length l_c , according to:

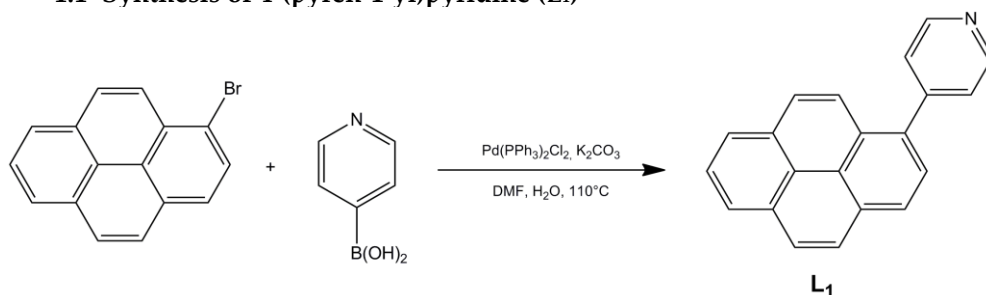
$$G(S) = \frac{1}{l_c} \left[A + \sqrt{\frac{I_{2\omega}(S)}{I_{2\omega}(0)}} \frac{E(0)}{E(S)} + B \right] 10^{-12}$$

where $I_{2\omega}$ is the intensity of the harmonic and E is the amplitude of the electric field (S being the solution of the chromophore and 0 the solvent; A and B are constants depending on the solvent and the cell windows. The microscopic γ_{EFISH} value is then inferred from the macroscopic susceptibilities of the solvent $\Gamma(0)$ and of the solute $\Gamma(S)$, according to:

$$\gamma_{\text{EFISH}} = \frac{M}{\rho N_A f x} [(1+x)\Gamma(S) - \Gamma(0)]$$

where N_A is the Avogadro's number, M the molecular weight of the compound, ρ the density of the solvent, x the molar fraction of the compound, and f a local field correction factor.

1.1 Synthesis of 4-(pyren-1-yl)pyridine (**L**₁)

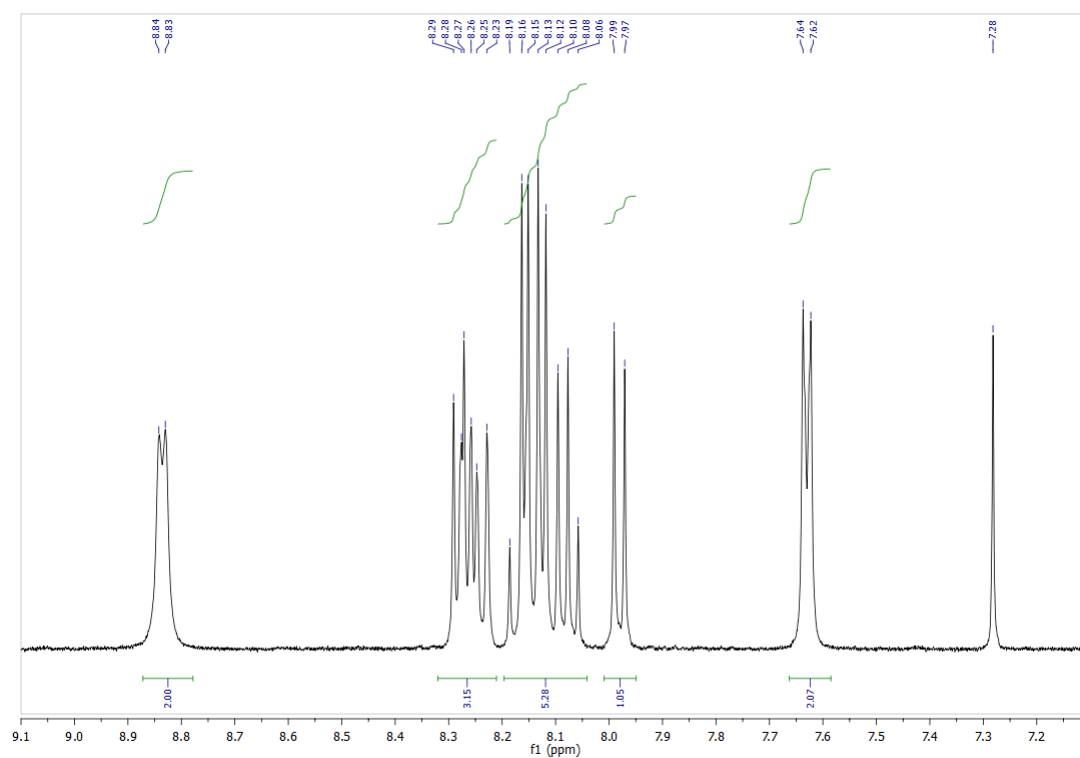
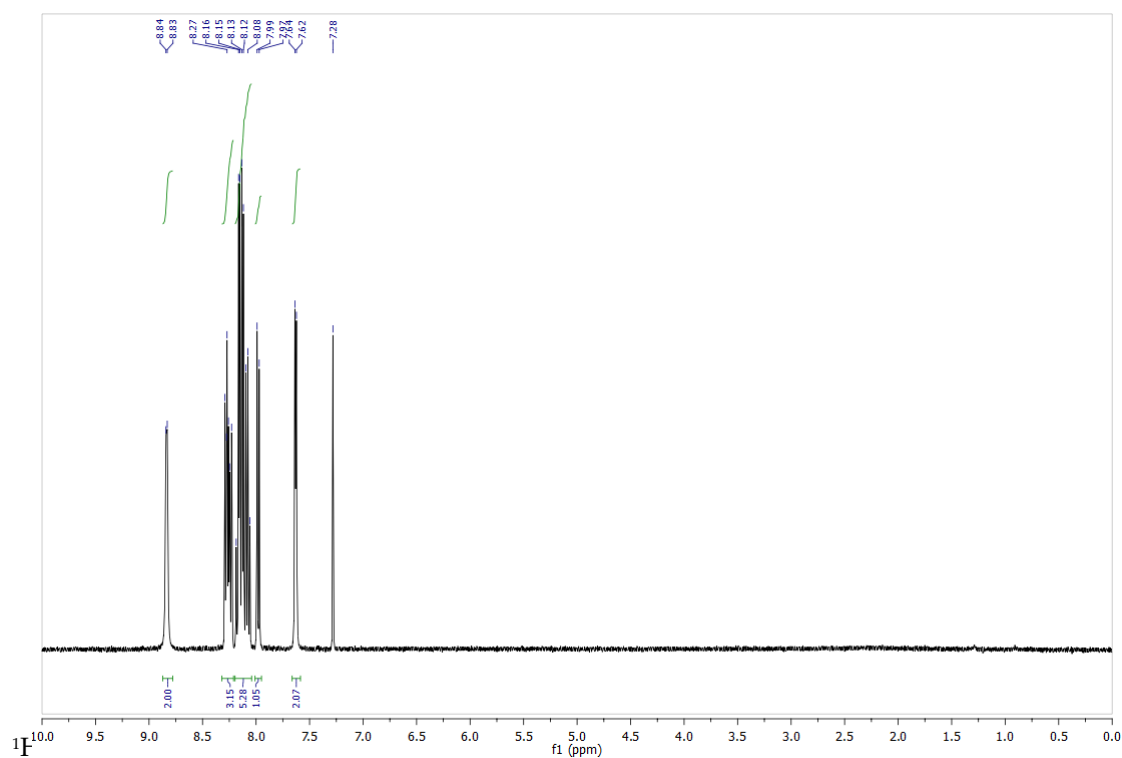


A 25mL Schlenk flask with a magnetic stirrer was loaded with 1-bromopyrene (300 mg, 1.07 mmol, 1 eq), 4-pyridinylboronic acid (180 mg, 1.46 mmol, 1.35 eq), Pd(PPh₃)₃Cl₂ (75 mg, 0.107 mmol, 0.1 eq), K₂CO₃ (590 mg, 4.27 mmol, 4 eq), N,N-dimethylformamide (5 mL) and water (1 mL). The mixture was heated one night at 110°C under nitrogen atmosphere.

The reaction mixture was added with 100 mL of CH₂Cl₂, stirred for 10 minutes and filtered on a Buchner. After washing 3 times with water (3x60 mL), the organic phase was dried over Na₂SO₄ and evaporated to dryness. Chromatography on silica gel (3% MeOH in CH₂Cl₂) afforded the pure product which was further crystallized from a CH₂Cl₂/hexane solution (197 mg, yield 66%).

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CH₂Cl₂/hexane solution.
¹H NMR data (400 MHz, CDCl₃, 298 K, δ, ppm): 8.83 (d, 5.8 Hz, 2H), 8.28 (d, 7.9 Hz, 1H), 8.28-8.23 (m, 2H), 8.19-8.06 (m, 5H), 7.98 (d, 7.9 Hz, 1H), 7.63 (d, 5.8 Hz, 2H).

¹H NMR of L₁ in CDCl₃



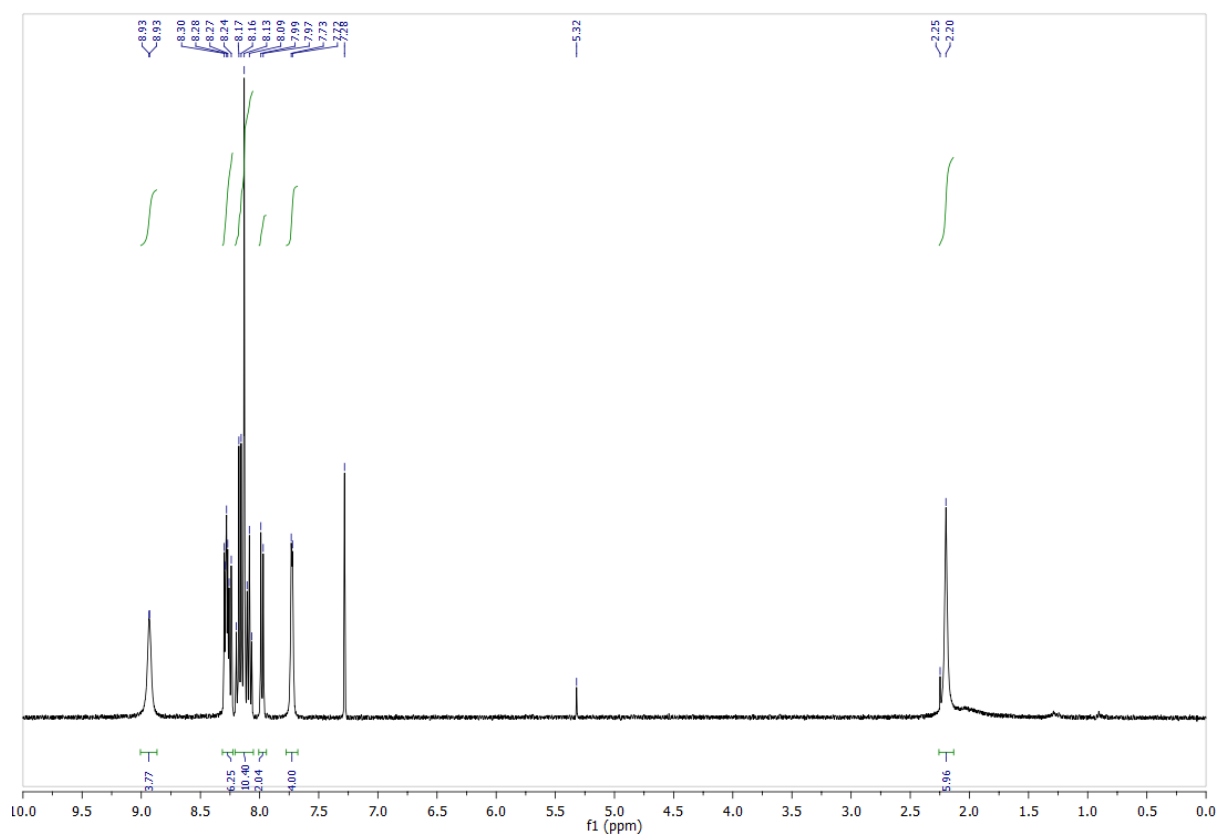
1.2 Synthesis of $[\text{Zn}(\text{CH}_3\text{CO}_2)_2(\text{L}_1)_2]$ (ZnL_1)

In a two-necked flask (100 mL) $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ (30 mg, 0.163 mmol, 1 eq) was kept under vacuum (10^{-2} Torr) for 3 h at 100 °C and then added with anhydrous CH_2Cl_2 (30 mL) and L_1 (107 mg, 0.383 mmol, 2.3 eq). The mixture was stirred overnight in the dark under N_2 . After evaporation of the solvent the product was obtained by crystallization from a CH_2Cl_2 /hexane solution. Crystals suitable for X-ray diffraction were collected by slow evaporation of a CH_2Cl_2 /MeOH solution.

Anal. Found. (calcd.): C, 73.68 (74.45); H, 4.47 (4.35); N, 3.57 (3.77).

^1H NMR data (400 MHz, CDCl_3 , 298 K, δ , ppm): 8.93 (d, br, 4H), 8.30-8.24 (m, 6H), 8.20-8.07 (m, 10H), 7.98 (d, 7.9 Hz, 2H), 7.72 (d, 4.3 Hz, 4H), 2.20 (6, 6H).

^1H NMR of ZnL_1 in CDCl_3



1.3 Synthesis of $[\text{CuI}(\text{L}_2)]_n$ (CuL_2)

A saturated aqueous solution of KI is added to solid CuI. The resulting mixture is filtered and transferred into a vial. L_2 (15 mg, 0.050 mmol) dissolved in CH_3CN (2 mL) is added to 4 mL of this solution. Crystals suitable for single crystal X-ray diffraction are obtained by slow evaporation of the reaction mixture.

Anal. Found. (calcd.): C, 55.77 (55.49); H, 3.50 (3.44); N, 2.89 (2.81).

^1H NMR data (400 MHz, DMSO, 298 K, δ , ppm): 8.43 (d, 9.2 Hz, 1H), 8.29 (dd, 7.4 and 7.2 Hz, 2H), 8.22 (dd, 9.6 and 8.1 Hz, 2H), 8.14 (s, 2H), 8.07 (dd, 7.6 and 7.6 Hz, 2H), 7.94 (d, 7.8 Hz, 1H), 7.60 (s, broad, 2H), 3.68 (dd, 7.5 and 8.2 Hz, 2H), 3.09 (dd, 6.8 and 7.2 Hz, 2H).

^1H NMR of CuL_2 in DMSO

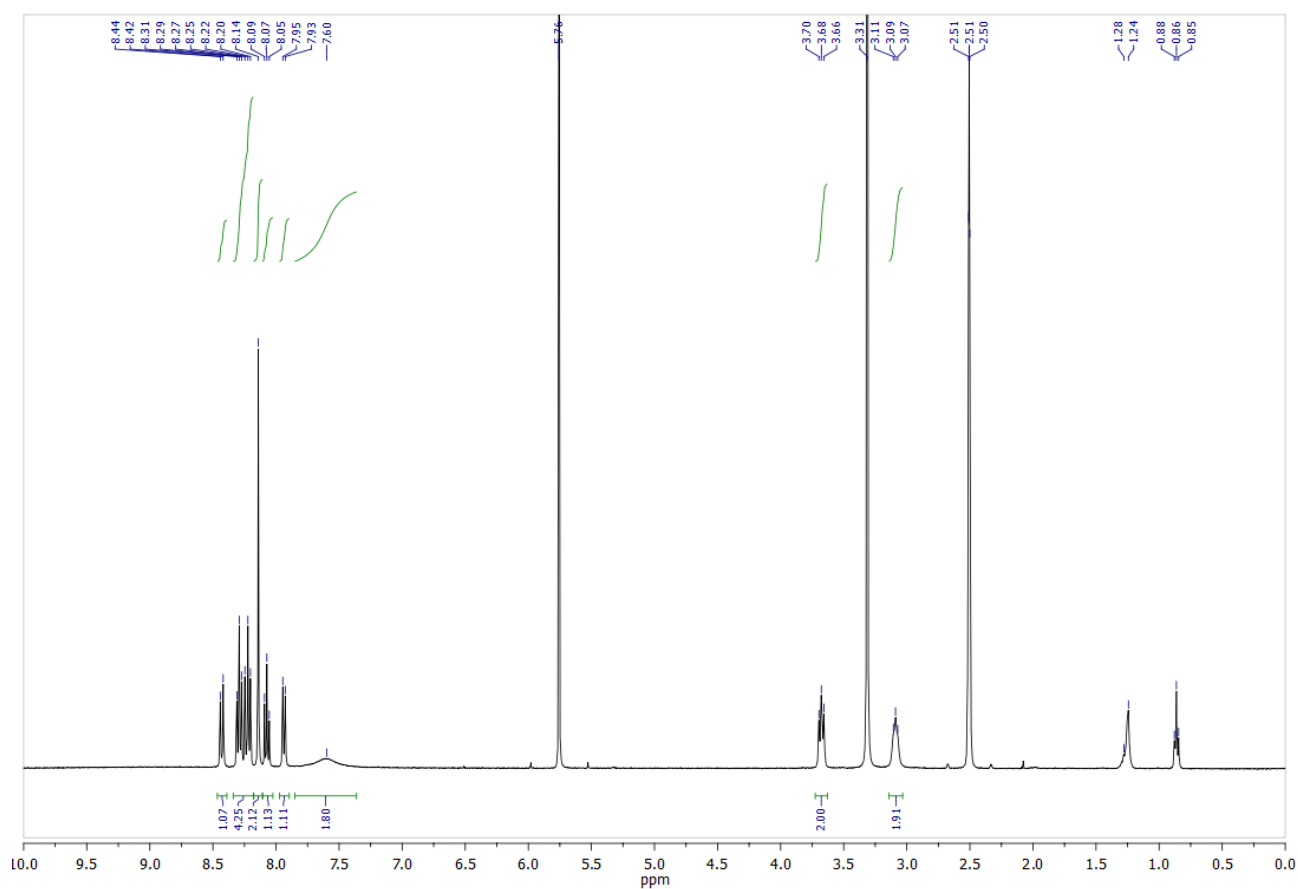


Figure S1. Expanded region of ^1H NMR spectra of **L**₁ (black) and **ZnL**₁ (red); 400 MHz, CDCl_3 , 298 K.

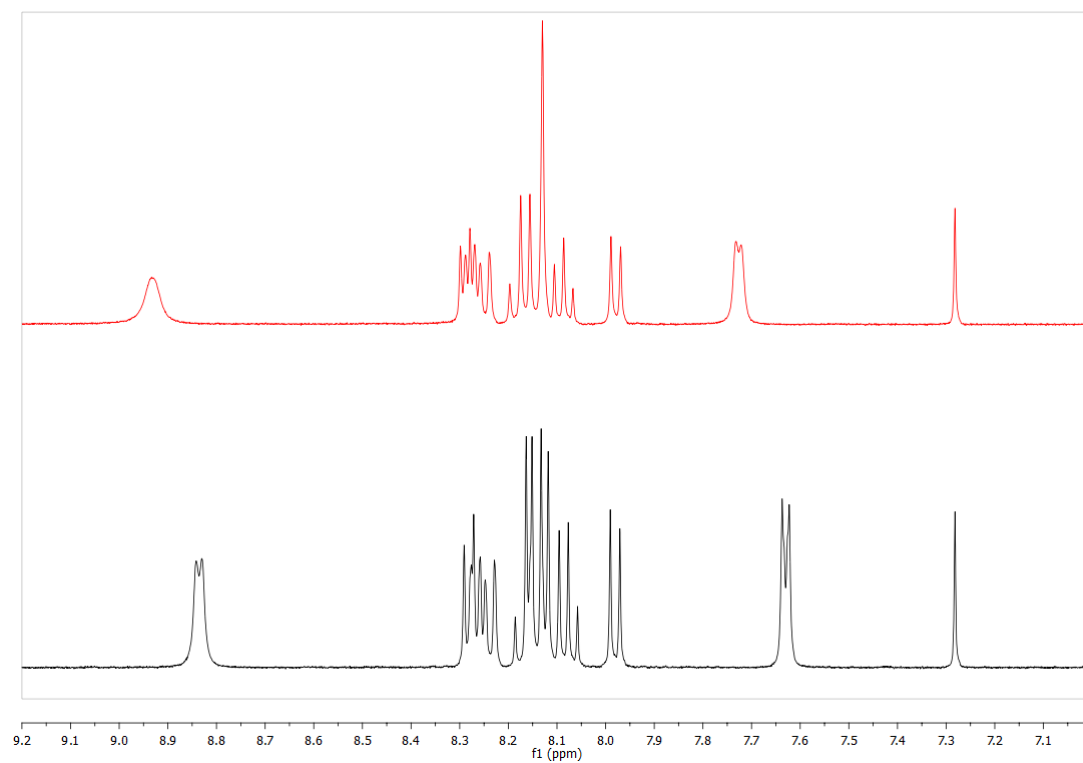
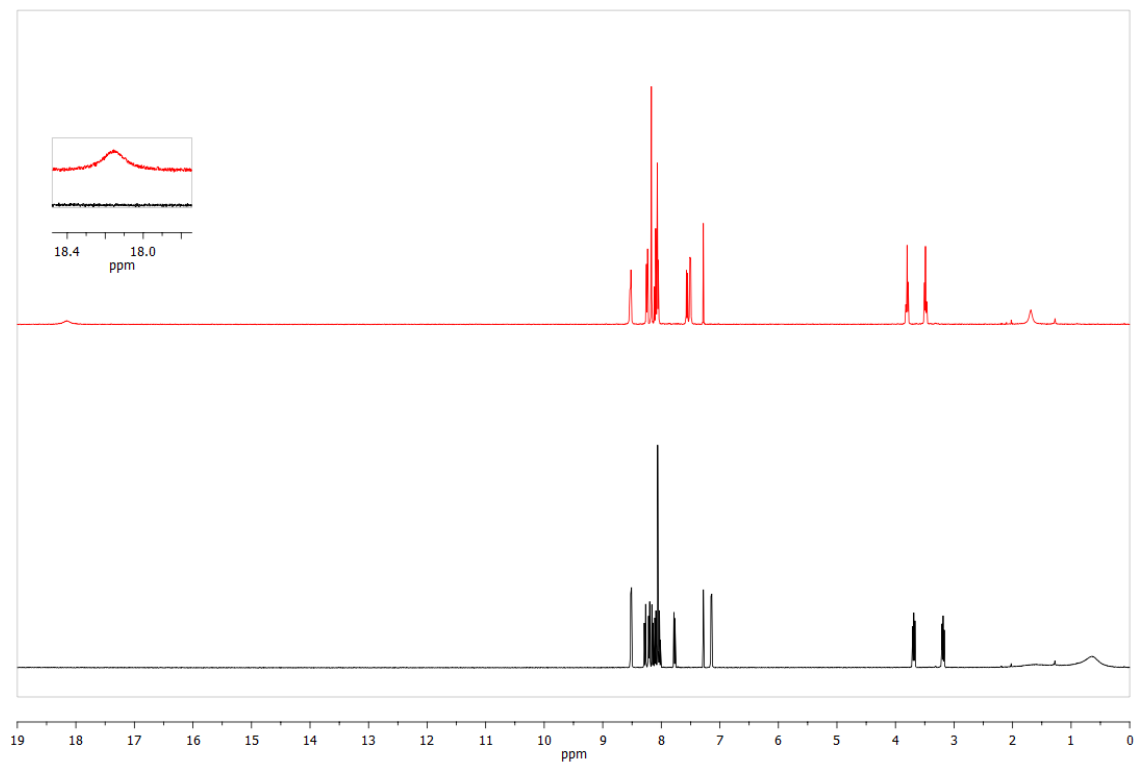


Figure S2. ^1H NMR spectra of **L2** (black) and **[L2H]⁺** (red); 400 MHz, CDCl_3 , 298 K.



Expanded region of ^1H NMR spectra of **L2** (black) and **[L2H]⁺** (red); 400 MHz, CDCl_3 , 298 K.

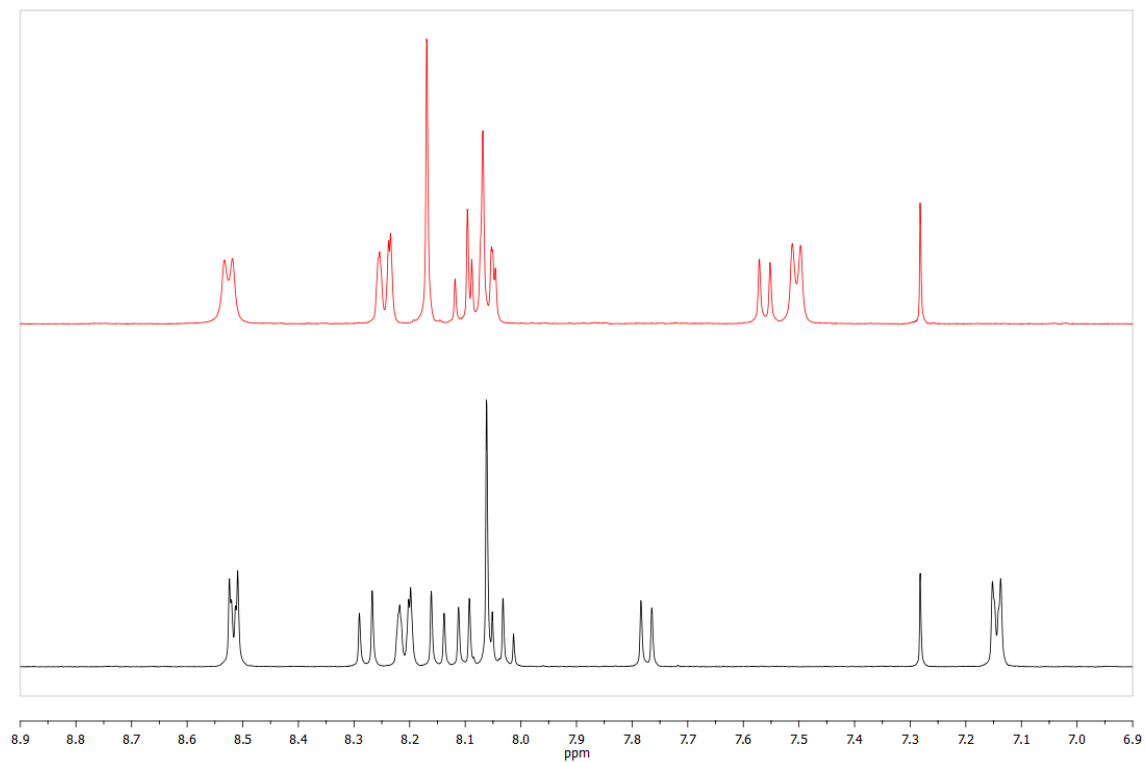
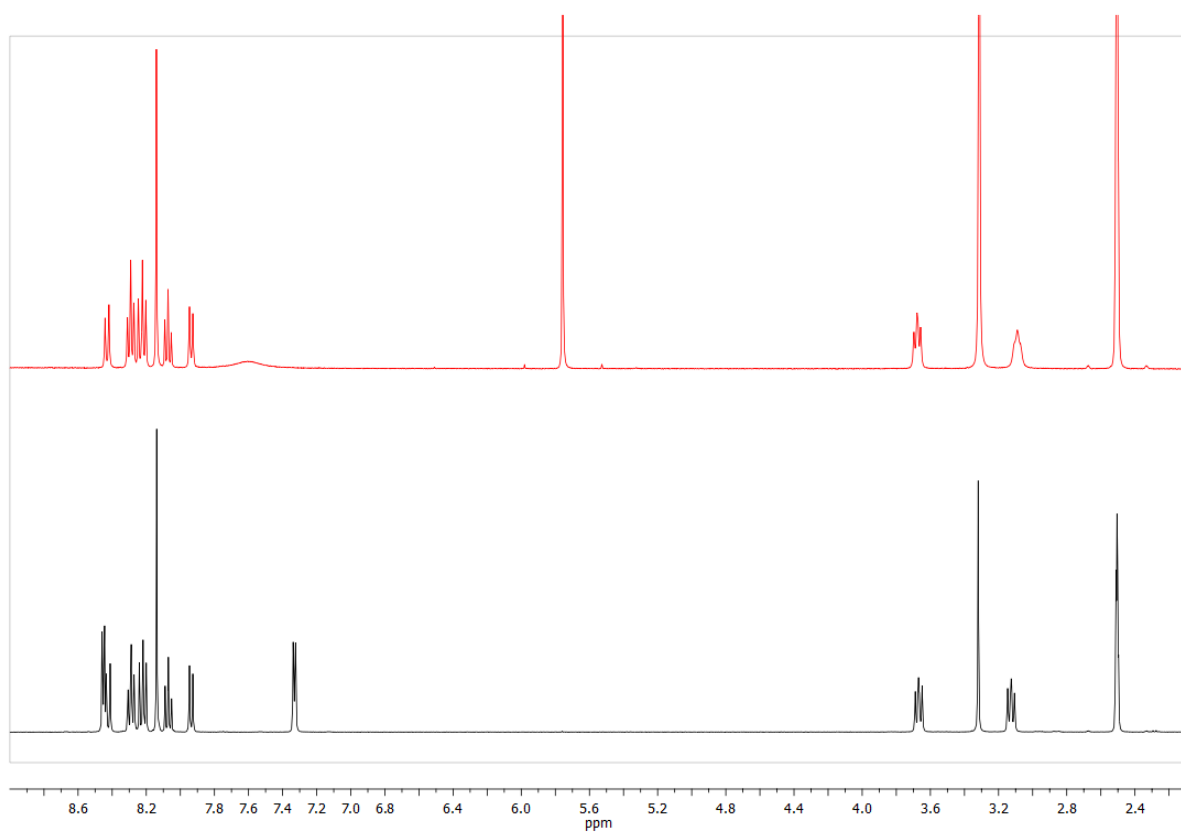


Figure S3. ^1H NMR spectra of **L2** (black) and **CuL2** (red); 400 MHz, DMSO, 298 K.



Expanded region of ^1H NMR spectra of **L2** (black) and **CuL2** (red); 400 MHz, DMSO, 298 K.

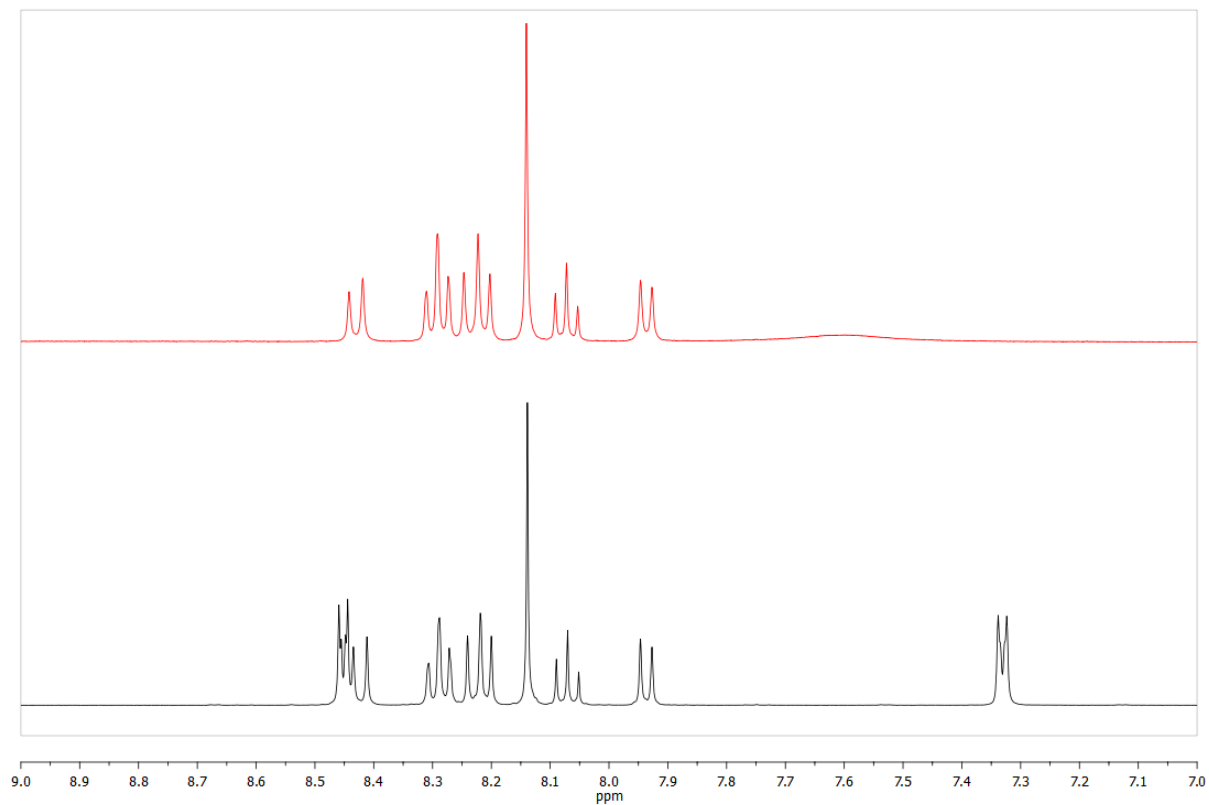


Figure S4. ORTEP view of **L1** with atom labelling scheme. Ellipsoids are drawn at 30 % probability level.

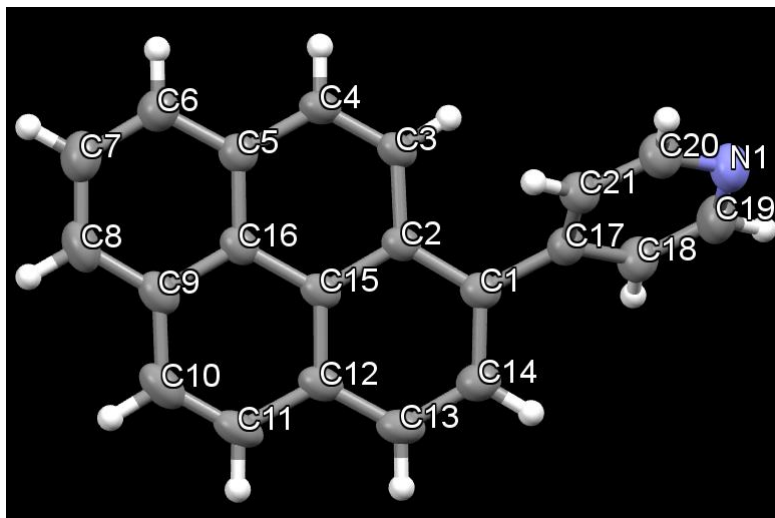


Figure S5. ORTEP view of the **ZnL1** with atom labelling scheme (only the main component of the disordered acetate group C24-C25-O3-O4 is shown). Ellipsoids are drawn at 30 % probability level.

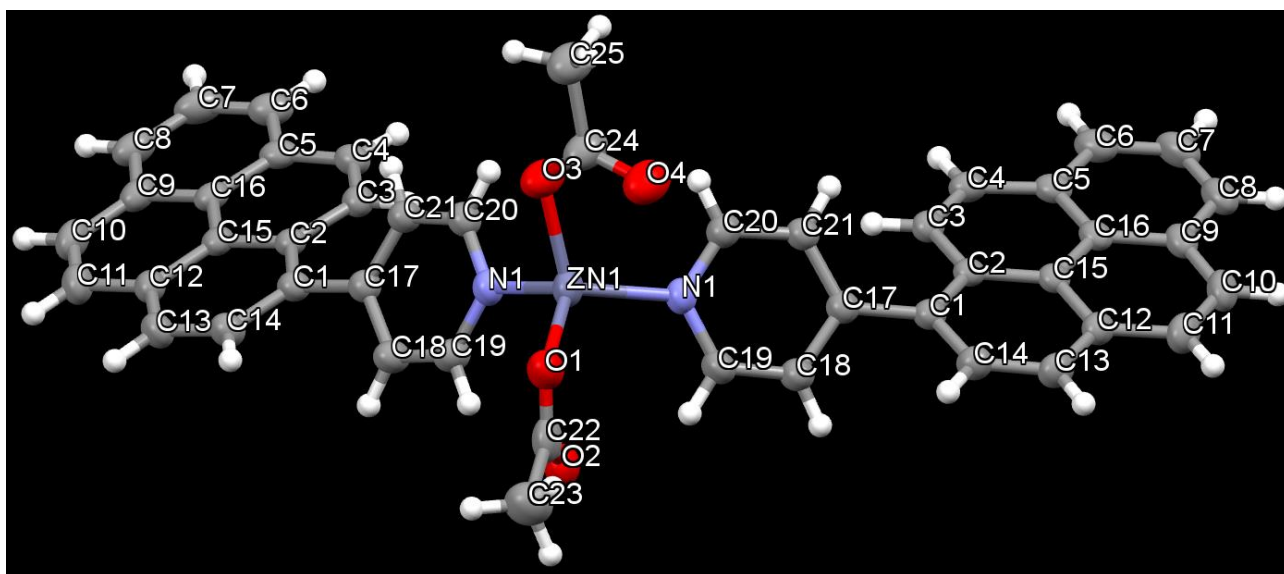


Figure S6. ORTEP view of **L2** with atom labelling scheme. Ellipsoids are drawn at 30 % probability level.

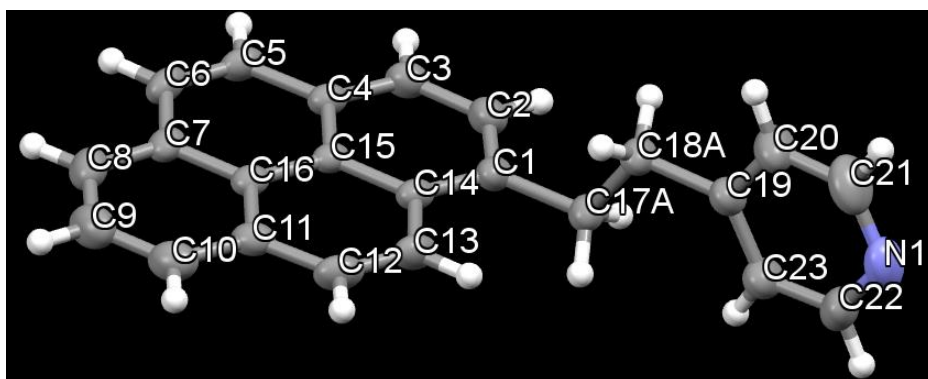


Figure S7. ORTEP view of **CuL2** with atom labelling scheme. Ellipsoids are drawn at 30 % probability level.

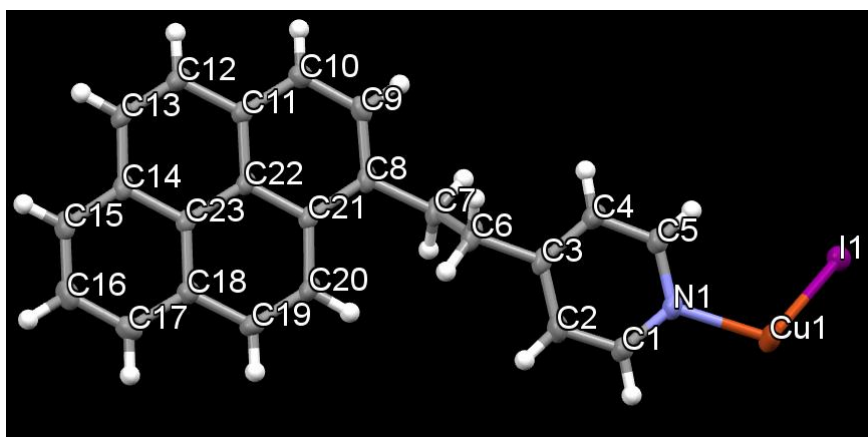


Table S1. Crystallographic data and structure refinement details for **L₁**, **ZnL₁**, **L₂** and **CuL₂**.

| | L₁ | ZnL₁ | L₂ | CuL₂ |
|---|------------------------------------|--|-----------------------------------|--------------------------------------|
| Chemical Formula | C ₂₁ H ₁₃ N | C ₄₆ H ₃₂ N ₂ O ₄ Zn | C ₂₃ H ₁₇ N | C ₂₃ H ₁₇ NCuI |
| Molecular weight | 279.32 | 742.10 | 307.38 | 497.82 |
| T(K) | 293(2) | 293(2) | 296(2) | 296(2) |
| Crystal system | Monoclinic | Orthorhombic | Triclinic | Monoclinic |
| space group | <i>P</i> 2 ₁ / <i>c</i> | <i>Pnma</i> | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> |
| a(Å) | 12.2207(13) | 12.5192(9) | 8.2054(10) | 20.4752(9) |
| b(Å) | 8.2084(9) | 24.7373(18) | 9.7248(12) | 4.5020(2) |
| c(Å) | 14.7380(16) | 11.2498(8) | 10.4571(12) | 20.2080(9) |
| α(°) | 90 | 90 | 85.133(2) | 90 |
| β(°) | 105.697(2) | 90 | 79.400(2) | 103.158(1) |
| γ(°) | 90 | 90 | 74.341(2) | 90 |
| V(Å ³) | 1423.3(3) | 3484.0(4) | 789.21(16) | 1813.85(14) |
| Z | 4 | 4 | 2 | 4 |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.304 | 1.415 | 1.293 | 1.823 |
| μ (mm ⁻¹) | 0.072 | 0.755 | 0.075 | 2.912 |
| Crystal size (mm) | 0.40 x 0.17 x 0.01 | 0.45 x 0.12 x 0.05 | 0.50 x 0.20 x 0.08 | 0.35 x 0.15 x 0.05 |
| 2θ _{max} , ° | 55.1 | 52.8 | 54.3 | 64.5 |
| No. of measured, independent, observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 31615 / 3274 / 1561 | 50099 / 3646 / 2709 | 12804 / 3494 / 2140 | 36089 / 6174 / 4762 |
| (<i>R</i> _{int})/(<i>R</i> _σ) | 0.0724 / 0.0425 | 0.0404 / 0.0206 | 0.0233 / 0.0200 | 0.0275 / 0.0203 |
| data/restraints/params | 3274 / 0 / 199 | 3646 / 123 / 300 | 3494 / 0 / 236 | 6174 / 0 / 235 |
| R[<i>F</i> ² > 2σ(<i>F</i> ²)], wR(<i>F</i> ²), S | 0.0543, 0.1669, 0.986 | 0.0517, 0.1629, 1.018 | 0.0494, 0.1530, 1.042 | 0.0333, 0.0844, 1.023 |
| Δρ _{max} , Δρ _{min} (e Å ⁻³) | 0.155, -0.127 | 0.465, -0.302 | 0.169, -0.182 | 1.696, -1.892 |

References

- [S1] Sankaran, N. B.; Das, A.; Samanta, A. Interaction between a pyridyl and a naphthyl/pyrenyl moiety in covalently linked systems. *Chem. Phys. Lett.* **2002**, *351*, 61-70, DOI. [https://doi.org/10.1016/S0009-2614\(01\)01366-5](https://doi.org/10.1016/S0009-2614(01)01366-5).
- [S2] Ledoux, I.; Zyss, J. Influence of the Molecular Environment in Solution Measurements of the Second-Order Optical Susceptibility for Urea and Derivatives. *Chem. Phys.* **1982**, *73*, 203-213, DOI. [https://doi.org/10.1016/0301-0104\(82\)85161-6](https://doi.org/10.1016/0301-0104(82)85161-6).